High loads of rare earth single-atom lanthanum anchored carbon nitride with special double-layer coordination structure for efficient photocatalysis

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ABSTRACT

A special two-layer coordination configuration anchored single-atom La (SALa) catalyst is synthesized to realize the effective separation of electrons in space and efficient active sites for the activation of O_2 to produce more active species. The special SALa microenvironment is obtained by a novel and facile reduction method that avoids the formation of rare earth oxides and the concentration of loaded SALa (10.34 wt%) exceeds that in most previous studies. The photodegradation test results show that antibiotics are almost completely removed within 30 min by SALa/CN. The first-order kinetic constant of SALa/CN (0.10661 min^{-1}) is approximately 9.81 times higher than that of 3DA-CN (0.01087 min^{-1}). SALa can be considered as a bridge to transfer electrons and $\bullet O_2^-$, $^1O_2$ and h^+ are the main active species to degrade tetracycline into some pollution-free small molecules. This work provides an efficient rare earth single-atom catalyst activity strategy possessing certain potential in practical applications.

1. Introduction

Many kinds of diseases triggering human beings can be effectively treated with antibiotics and the breeding industry excessively depends on them. What worries people is that the majority of antibiotics cannot be completely absorbed by the human body. Approximately 90% of antibiotics are discharged into the environment in the form of the origin or metabolites of the body [1–3]. Moreover, the continuous pollution of antibiotics poses a great threat to the ecological environment and human health. Self-degrading antibiotics using solar energy under natural conditions is a promising technology to solve the above problems, which has the advantages of strong oxidation capacity, easy implementation and green environmental protection [4–6]. In the process of self-degradation, the photocatalyst is irradiated by an energy greater than or equal to the band gap of the photocatalyst, triggering the production of photogenerated electrons (e-) and holes (h+) with certain energy [7,8]. The e- and h+ are migrated in the interior and interface of the photocatalyst and undergone redox reactions with substances adsorbed on the surface or in solvents, consequently, the active species are produced to act on antibiotics [9,10]. Regarding photocatalytic technology, the design of high-performance materials plays a decisive role in the application of photocatalytic treatment for antibiotics.

For traditional nanomaterials, most of the inner atoms cannot participate in the redox reaction and only the exposed surface atoms are involved in catalytic reactions, which has certain limitations for the utilization of active atoms. Single atom catalysts (SACs) have 100% atomic utilization providing the conditions for a single atom to fully contact the target molecules [11,12]. To date, many SACs with excellent performance have been reported in the field of photocatalysis. Wang et al. [13] proposed the photoinduction of single-atom Cu decorated on UiO-66-NH$_2$ for enhanced photocatalytic reduction of CO_2 forming liquid fuels. Sun et al. [14] constructed single-atom Ag decorated tremella-like g-C$_3$N$_4$, which significantly improved the photocatalytic efficiency of tetracycline (TC) removal. Single-atom Pt confined by the interlayer nanospace of g-C$_3$N$_4$ for efficient photocatalytic hydrogen evolution was researched by Quan's group [15]. Consequently, SACs can

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provide the large number of well-defined active sites for the reaction, which can maximize the catalytic activity of the photocatalyst [16–18].

Selecting suitable support material is the key step in obtaining SACs. Graphitic carbon nitride (g-C_3N_4) is a typical polymer semiconductor in which the C and N atoms in the structure form a highly delocalized π conjugated system with sp^2 hybridization. g-C_3N_4 has anions that co-ordinate with metal atoms and can design good coordination structures [19–21]. Gao et al. [22] explored the mechanism of single-atom Pd and Pt loading on g-C_3N_4 materials with excellent CO_2 reduction activity by DFT calculations. Zou's group [12] developed a highly active and stable SAAg/g-C_3N_4 sample, which can reduce the H_2 evolution barrier, expand the light absorption range and improve the charge transfer efficiency. Xiao et al. [23] established the engineering of single-atom Cu bonded with compositional N of g-C_3N_4, achieving highly effective charge transfer channels. Moreover, g-C_3N_4 with a two-dimensional nanosheet structure is prone to agglomeration, whereas hierarchical g-C_3N_4 can solve the agglomeration phenomenon and provide more active sites for the reaction. Therefore, it is expected that the SACs with hierarchical g-C_3N_4 as support material have excellent carriers separation efficiency, fantastic visible light absorption ability and high photocatalytic performance.

Among all kinds of SACs, rare earth SACs can realize efficient utilization and greatly improve the added value of rare earth resources. Rare earth elements have unique electronic, optical and magnetic properties arising from the spin-orbit coupling of the 4 f and valence orbitals. In addition, benefiting from their electronic properties and large radii, rare earth atoms frequently present stable high-coordination structures which increase the thermal stability. Several rare earth SACs have recently been developed and exhibit excellent performance in various catalysis processes. Ma et al. [24] reported that praseodymium (Pr) SAC encapsulated by g-C_3N_4 substrate with a loading content of 21.05 wt% exhibited high photoreduction performance of CO_2 to CH_3OH. Shui's group [25] reported the synthesis of yttrium (Y, 0.38 wt%) and scandium (Sc, 1.24 wt%) SACs on N-doped carbon support for N_2 and CO_2 reduction reactions. Sun et al. [26] reported highly coordinated cerium (Ce, 0.26 wt%) single-atom sites on g-C_3N_4 nanosheets for efficient photocatalytic amine oxidation and H_2O splitting into H_2. However, the synthesis and application reports of rare earth SACs are still very limited. The 4 f orbital of lanthanide (La) is not fully occupied, and the 5 f orbital is vacant, which can provide effective electron capture capability, thus improving the separation efficiency of photoexcited carriers [27,28]. As a representative lanthanide compound, La has a shallow potential well induced by its full electron configuration, which can effectively regulate the electronic structure and catalytic activity of photocatalysts. Therefore, La has attracted extensive attention from researchers. Jia et al. [29] constructed La-doped $ZnIn_2S_4$ microspheres promoting the separation efficiency of electrons and holes. Jing et al. [30] prepared direct Z-scheme red g-C_3N_4/rod-like $LaVO_4$ composites with a remarkable enhancement of photocatalytic behaviour. Xie et al. [31] synthesized La_2O_3-modified g-C_3N_4 material with high specific surface area, extended light absorption and enhanced carriers separation efficiency. The above studies only introduced La as a doping element. However, single-atom La (SALa) catalysts have rarely been studied. Therefore, it is very valuable to obtain SALa material by simple and effective method. The nature of photocatalytic mechanism related to the electronic structure of rare earth single atom requires in-depth and systematic study at the atomic and electronic levels.

Herein, high loading of rare earth SALa on agaric-like g-C_3N_4 (3DA-CN) was prepared by solvothermal reduction combined with high-temperature reduction method achieving the maximum utilization rate of rare earth metal atoms and the utilization of effective added value. The new coordination configuration (two-layer structure) of SALa/CN is obtained, which reduces the transfer barrier of photogenerated electrons, and thus significantly increases the photocatalytic activity. The local environment of SALa/CN has been thoroughly studied by aberration-corrected high-angle annular dark field STEM (AC-HAADF-

STEM), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The charge density distribution between SALa and 3DA-CN was studied by density functional theory (DFT) calculations. The time-resolved photoluminescence indicates that the main form of electrons transition for SALa/CN is nonradiative transition and that electrons mainly participate in the photocatalytic reaction. The steady-state fluorescence and photoelectric chemistry tests proved that SALa/CN has excellent carriers separation efficiency. In addition, SALa/CN was used in the photocatalytic removal of antibiotics showing excellent efficiency. The photocatalytic mechanism of the synergistic interaction between the electronic structure of rare earth SALa and 3DA-CN has been studied deeply and systematically.

2. Experimental section

2.1. Chemicals

Melamine ($C_3H_6N_6$), cyanuric acid ($C_3H_3N_3O_3$), lanthanum nitrate (La(NO$_3$)$_3$), ascorbic acid ($C_6H_8O_6$), isopropanol (C_3H_8O), 2,2,6,6-tetra-methyl-1-piperidinyloxy ($C_9H_{18}NO^*$), 2,2,6,6-tetramethyl-4-piperidone ($C_9H_{17}NO$), 5,5-dimethyl-1-pyrroline N-oxide ($C_6H_{11}NO$) and catalase (CAT, 2000–5000 U/mg protein) were purchased from Aladdin Reagent. Acetonitrile (C_2H_3N), nitric acid (HNO$_3$), lanthanum oxide (La_2O_3), tetracycline ($C_{22}H_{24}N_2O_8$), oxytetracycline hydrochloride ($C_{22}H_{24}N_2O_9 \cdot HCl$), doxycycline hydrochloride ($C_{24}H_{30}N_2O_9 \cdot HCl$), ethanol ($C_2H_6O$), acetic acid ($C_2H_4O_2$) and sodium sulfate ($Na_2SO_4$) were supplied by Sinopharm Chemical Reagent. Ethylenediaminetetra-acetic acid disodium salt ($C_{10}H_{14}N_2Na_2O_8$) and L-tryptophan ($C_{11}H_{12}N_2O_2$) were purchased from Jiuding Chemical Co., Ltd. All reagents were standard-grade analytical. Nitrogen (N_2) and hydrogen (H_2) were purchased from Nanjing Special Gas Co., Ltd. Deionized water was provided by a local water purification company.

2.2. Materials preparation

2.2.1. Synthesis of three-dimensional agaric-like carbon nitride (3DA-CN)

The 3DA-CN material was prepared by one-step direct calcination method. Specifically, 1:2:2 molar ratios of acetonitrile, ethanol and water were used to form a uniform mixed solution, and then melamine (1.26 g) and cyanic acid (1.29 g) were added to the above solution and stirred at room temperature for 4 h. After that, they were loaded into a high-pressure reaction kettle and kept at 110 °C for 12 h. After the reaction was cooled, the white supramolecular precursor was collected by centrifugation. The white product was dried and fully ground into fine powder and then put into the crucible and calcined directly in a muffle furnace, and the yellow powder was obtained, namely 3DA-CN.

2.2.2. Synthesis of single-atom lanthanum dispersed 3DA-CN (SALa/CN)

3DA-CN (0.2 g) was added to the deionized water (120 mL), and 3DA-CN was dispersed by ultrasound for 2 h. Then, La(NO$_3$)$_3$ (0.1 M, 15 mL) solution and an appropriate amount of phenol were added and ultrasonicated for 4 h under dark conditions. The mixed solution was put into the reaction kettle at 160 °C for 16 h. The reaction product was freeze-dried and then fully ground to obtain pale yellow fine powder (La ion/CN). The La ion/CN was put into the porcelain boat and calcined at 400 °C with H_2 and N_2 (V (H_2): V (N_2) = 3:17) for 4 h to obtain the product. Finally, the product was soaked and washed in water and ethanol to obtain the final sample (SALa/CN). A schematic illustration of the formation process of SALa/CN is depicted in Scheme 1.

2.3. Device characterization

The details of the device characterization are provided in the supporting information (SI).
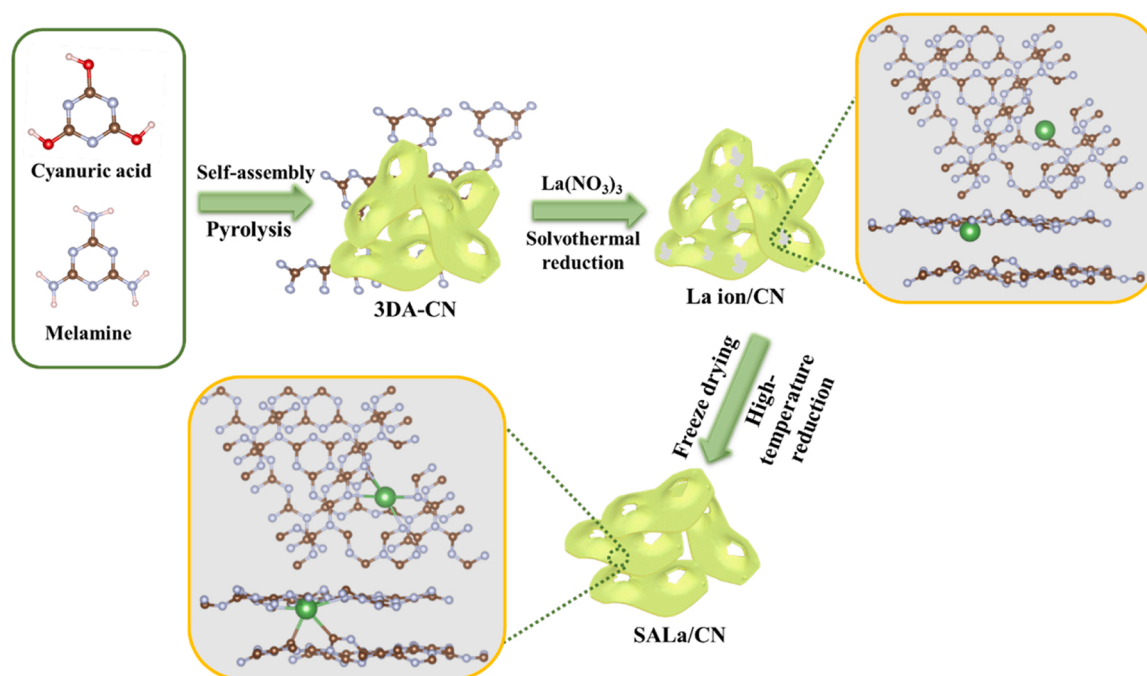
Scheme 1. Schematic illustration of the formation process of SALa/CN.

2.4. Photocatalytic performance evaluation experiments

The photocatalytic performance of the as-prepared materials was evaluated by photocatalytic degradation TC. Specifically, 100 mL TC (20 mg/L) was added into the quartz reactor, and then 20 mg photocatalyst was added. The geometry of the reactor is cylindrical (outer height: 92 mm, external diameter: 70 mm, inner height: 78 mm, internal diameter: 46 mm). The reactor is designed with a double-layer jacket that is filled with circulating water (supplied by controlled temperature water circulation system) to maintain a constant temperature (25 °C) for the photocatalytic reaction. The dark reaction was performed under magnetic stirring for 30 min to achieve adsorption equilibrium and then the reaction was transferred into the photocatalytic system and the aeration device was started. The light source was 300 W Xenon lamp ($\lambda \geq 420$ nm), and reaction products were taken every 5 min. The liquid part of the reaction product was collected by centrifugation and filtration. The corresponding absorbance of the liquid was tested under UV–vis spectrophotometer at 357 nm. To ensure the reliability of the results, the same experiments were carried out three times. The Lambert—Beer law is used to calculate the degradation efficiency. To demonstrate the suitability of SALa/CN, photocatalytic removal of oxytetracycline and doxycycline was performed using the same experimental procedure as described above. The stability and effectiveness of SALa/CN were proven by using cycling experiments and simulating real water environment experiments.

3. Results and discussion

3.1. Morphology and microstructure analyses

The morphology and microstructure of 3DA-CN and SALa/CN were characterized by scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1a, 3DA-CN shows an agaric-like structure with pores. To more clearly study the morphology of 3DA-CN, the scale of the image is enlarged in Fig. 1b. The morphology of 3DA-CN has a regular hierarchical structure consisting of undulating slices approximately 400 nm in size, providing the possibility of more active sites and multichannel electron transfer for the

reaction [32]. Moreover, a certain pore structure of 3DA-CN is found, which is conducive to mass transfer and diffusion to improve the catalytic activity [33]. It can be seen in Fig. 1c that the microstructure of 3DA-CN is more clearly displayed and presented almost transparent meaning thin thickness. The 3DA-CN shows an obvious three-dimensional structure similar to undulating agaric, which can short the distance of electrons transmission enhancing the separation efficiency of electrons and holes [34,35]. Moreover, the morphologies of SALa/CN are presented in Fig. 1d-e, which still maintain an agaric shape with unchanged pores. It indicates that the introduction of SALa does not change the morphology of 3DA-CN.

The tiny clusters or lanthanum-containing nanoparticles are not detected by TEM images (Fig. 1f-g), implying that La species are uniformly dispersed in the 3DA-CN matrix. Meanwhile, mapping images (Fig. 1 h) were used to analyze the elemental composition (C, N and La) of SALa/CN. It verifies that C, N and La are uniformly dispersed throughout the SALa/CN. Due to the limitation of the detection sensitivity for TEM, the existence of SALa could not be clearly seen, so we carried out Aberration-corrected high-angle annular dark field STEM (AC-HAADF-STEM) to research the SALa/CN. As shown in Fig. 1i-j, the white bright spots (marked in yellow circles) are SALa, which clearly shows that the high-loading SALa are uniformly dispersed on the 3DA-CN without aggregation into clusters and nanoparticles. The intensity profiles along lines 1 and 2 further confirm that the size of these spots ranged from 1 Å to 2 Å and that there is a distance between bright spots, implying that each white spot is an isolated SALa [36]. Simultaneously, the loading content of SALa up to 10.34 wt% was detected by inductively coupled plasma optical emission spectroscopy (ICP—OES). Subsequently, the SALa/CN catalyst was soaked in nitric acid (0.5 mol/L) and then washed with water and ethanol. The content of La was detected by ICP—OES and it was found that the content of La (10.31 wt%) in the catalyst was almost not reduced. It indicates that the SALa/CN catalyst does not contain La$_2$O$_3$ and La clusters. Rare earth elements easily combine with ambient oxygen to form oxides, so it is difficult to obtain high load of rare earth SACs. The loading of SALa prepared in this experimental system is 10.34 wt%, which is higher than that of most previous rare earth SACs studies (Table S1). Therefore, the single-atom catalyst with high-loading of SALa was successfully obtained, laying a
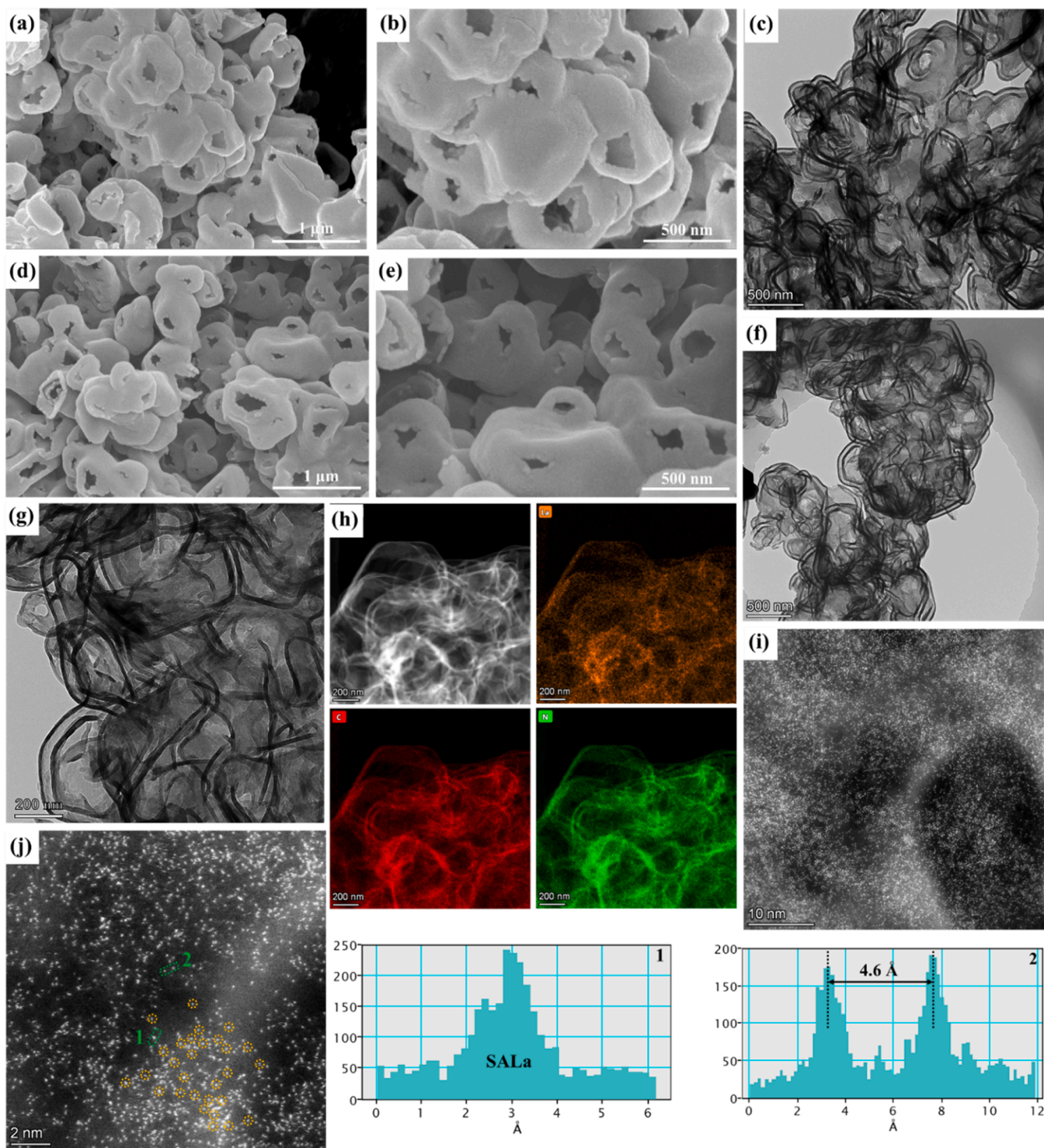
Fig. 1. (a, b) SEM images of 3DA-CN; (c) TEM image of 3DA-CN; (d, e) SEM images of SALa/CN; (f, g) TEM images of SALa/CN; (h) TEM with elemental mapping of SALa/CN; (i, j) AC-HAADF-STEM of SALa/CN.

foundation for the subsequent excellent photocatalytic activity.

3.2. Chemical state and structure analyses

To explore the chemical state of the as-prepared photocatalysts, X-ray photoelectron spectroscopy (XPS) was applied as a characterization technique and the results are shown in Fig. 2. An obvious new peak (marked in shadow) is observed in the full survey spectra of SALa/CN (Fig. 2a) compared with the survey spectra of 3DA-CN, which

demonstrates the coexistence of La, C and N elements. It indicates that La element was successfully introduced into 3DA-CN corresponding with the mapping results. The high-resolution La 3d spectra are revealed in Fig. 2b. The La 3d of La_2O_3 can be fitted into four peaks appearing at 834.9 eV, 838.6 eV, 851.8 eV and 855.4 eV, which correspond to La $3d_{5/2}$ and La $3d_{3/2}$. Interestingly, the La 3d peaks position of SALa/CN are shifted by 0.6 eV and toward the higher binding energy than the peak of La_2O_3, indicating that the electronic orbital state of SALa is different from that of La (III) in La_2O_3. That is, the coordination
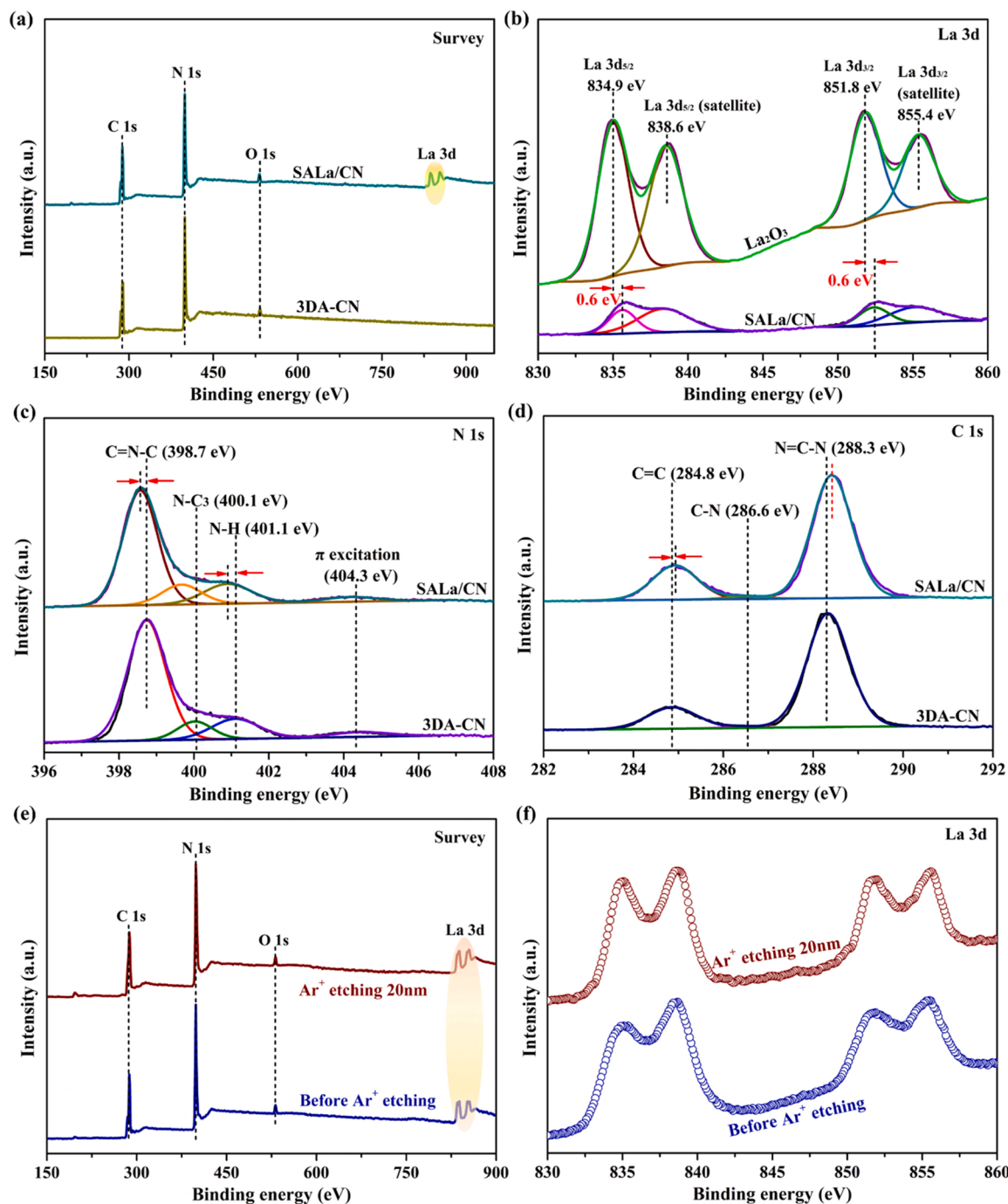
Fig. 2. (a) The XPS full survey spectra of 3DA-CN and SALa/CN; (b) La 3d of La_2O_3 and SALa/CN; (c) N 1 s and (d) C 1 s of 3DA-CN and SALa/CN; (e) the XPS full survey spectra and (f) La 3d of initial sample and Ar^+ etching 20 nm.

environment of La in SALa/CN is different from that of La (III). The specific coordination environment for SALa is illustrated later using X-ray absorption spectroscopy (XAS). Simultaneously, the N 1 s spectrum of 3DA-CN (Fig. 2c) exhibits four peaks, which are attributed to the C=N-C, N-C$_3$, N-H and π excitation positions at 398.7 eV, 400.1 eV, 401.1 eV and 404.3 eV, respectively. The N species of SALa/CN move to a lower binding energy direction relative to 3DA-CN. It suggests that there is a strong interaction between the SALa and 3DA-CN skeletons causing electrons to be transferred between them [15]. As depicted in Fig. 2d, three obvious peaks are located at 284.8 eV, 286.6 eV and 288.3 eV in the C 1 s spectrum of 3DA-CN, which are indexed to C=C, C-N and N = C-N bonds, respectively. The peak shape of C 1 s spectrum

also underwent a certain degree of change after the introduction of SALa, indicating an interaction between SALa and C atoms [37,38]. Therefore, SALa is successfully integrated into 3DA-CN and changes the electron cloud density of 3DA-CN. The distribution fitting of the O 1 s is presented in Fig. S1. The peak at 532.1 eV is attributed to the adsorption of H_2O from the environment on the material surface [39]. According to the survey spectrum analysis (Table S2), the mass ratio of SALa is 10.47 wt%. The consistent results of ICP—OES and XPS prove that SALa are not distributed on the catalyst surface. Meanwhile, the XPS argon ion etching experiment was implemented to further verify that the SALa is not distributed on the surface of 3DA-CN. As shown in Fig. 2e-f, argon ion etching at 20 nm still detected the characteristic peaks of La 3d with

the same intensity as the initial value and the corresponding analysis data (Table S3) suggest that the amount of La barely changed.

The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were performed to elucidate the electronic structure and coordination environment of SALa/CN. From the La L_3-edge XANES spectra in Fig. 3a, the white line intensity of SALa/CN is higher than that of La_2O_3, indicating that the average valence state of SALa is greater than $+3$ [40,41]. The valence state of SALa was also calculated as $+3.29$ by DFT calculations, which is consistent with the XANES results. The Fourier transformed (FT) k^3-weight EXAFS spectra at the La L_3-edge are applied to analyze the coordination environment of SALa (Fig. 3b). The FT-EXAFS spectrum of La_2O_3 was detected with a distinct peak at 2.08 Å, corresponding to La-O scattering. The peak of SALa/CN is located at 1.97 Å, which does not match the scattering path of La-O. The experimental value of La foil cannot be supplied because the chemical properties of lanthanum are too reactive. Therefore, the La foil was calculated using FEFF and the relevant calculation parameters are provided in the SI (Section 3). As a comparison, the La-La contribution is located at 3.23 Å in the La foil reference indicating the nonexistence of La-La in SALa/CN. Furthermore, a least-squares FT-EXAFS curve fitting of SALa/CN was obtained in Fig. 3c. The specific fitting parameters are presented in Table S4. The

results show that SALa coordinates with six N/C atoms on 3DA-CN. The corresponding EXAFS curves fitting in q-space and k-space are presented in Fig. S2. Subsequently, the possible models (Fig. S3-S4) were constructed by DFT calculations and the corresponding bond lengths are displayed in the diagram. It is deduced that the structure of SALa/CN is $DLaN_4C_2$ (double-layer coordination: four nitrogen and two carbon) according to the average coordination bond length (2.63 Å, Table S4). Therefore, a reasonable structural model is derived and embedded in Fig. 3c. We further calculated La L_3-edge XANES spectra for SALa/CN theoretically implemented in FDMNES software, confirming that the theoretical spectrum of $DLaN_4C_2$ is consistent with the experimental data (Fig. 3d). Moreover, the first coordination shell of SALa/CN is located between La-C and La-N in Fig. 3e, which is consistent with the results of the above reasoning model. EXAFS calculation results by FEFF of different coordination environments of SALa samples (Fig. 3f) show obvious characteristic peaks of higher shells. The other low intensity peaks in SALa/CN may be caused by higher shells or noise and do not corresponding to the peak of La_2O_3 [25,42]. According to the above analysis, the FT-EXAFS spectra further ruled out the presence of metallic La or La_2O_3 in the SALa/CN catalyst.

The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO adsorption is a powerful technique to distinguish
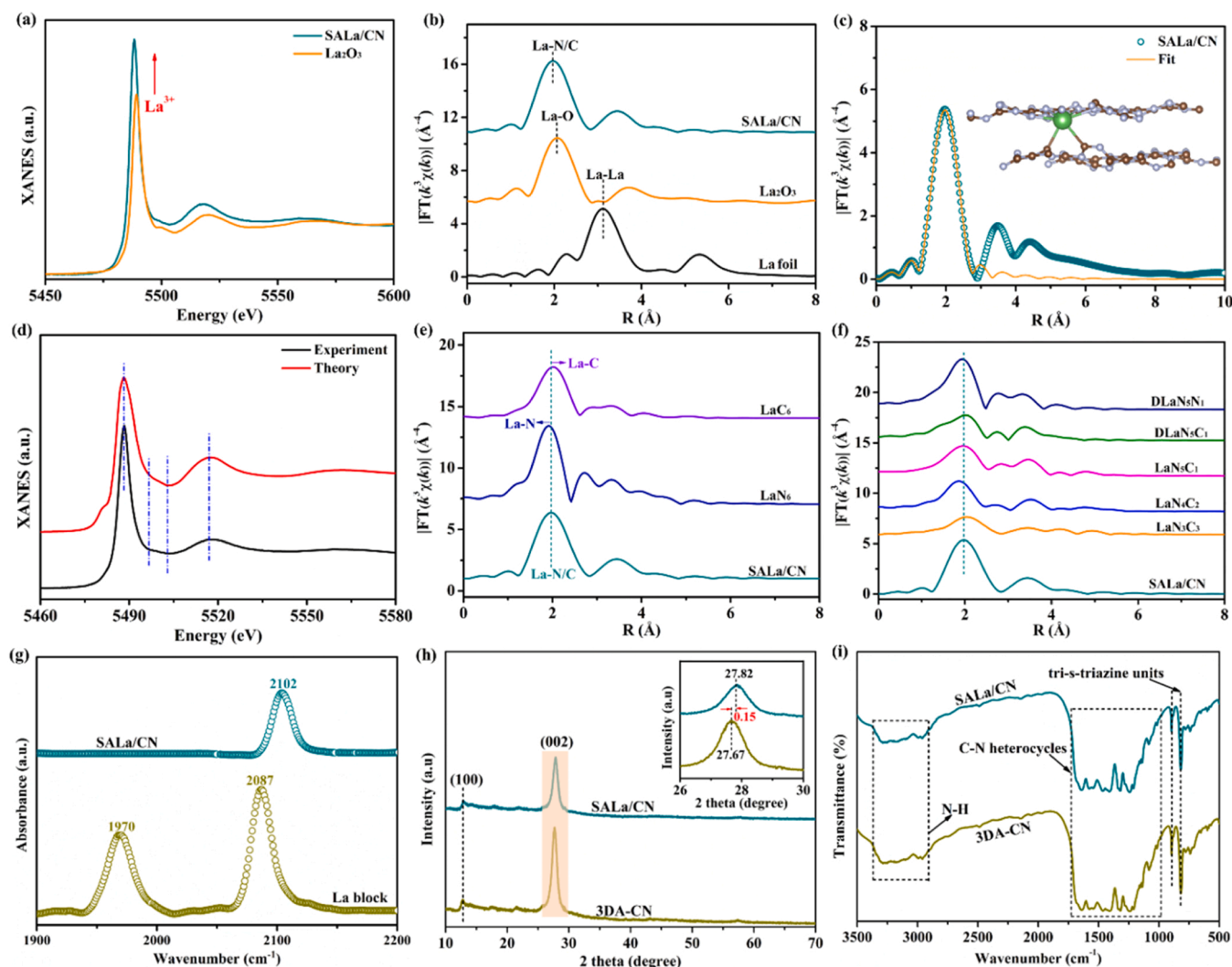

Fig. 3. (a) The normalized XANES spectra at the La L_3 edge of SALa/CN and La_2O_3; (b) the FT k^3-weight EXAFS spectra of La foil, La_2O_3 and SALa/CN; (c) EXAFS fitting curve of SALa/CN; (d) Comparison between the experimental XANES spectrum of SALa/CN and theoretical spectrum of $DLaN_4C_2$; (e, f) FEFF calculation results of different coordination environments of SALa samples; (g) in situ DRIFTS of CO adsorption spectra on the SALa/CN and La block; (h) the XRD patterns (insetting an enlarged version) and (i) FT-IR spectra of 3DA-CN and SALa/CN.

the single atom and aggregated sites. As shown in Fig. 3g, two distinct characteristic peaks are detected in the La block at 2087 and 1970 cm^{-1}, which are attributed to linear and bridge adsorption of CO, respectively. For the SALa/CN sample, only one characteristic peak at 2102 cm^{-1} is detected, corresponding to the linear adsorption peak of CO by SALa, suggesting that La species is atomically dispersed on the 3DA-CN support [43,44]. The crystalline structures of 3DA-CN and SALa/CN were detected by X-ray diffraction (XRD) and the corresponding XRD patterns are shown in Fig. 3h. Two distinct diffraction peaks at approximately 12.83° and 27.67° are found in 3DA-CN indexed as the (100) plane and (002) plane, respectively [45,46]. Specifically, the structural packing of tri-s-triazine motifs causes the (100) plane of 3DA-CN, and the (002) plane is caused by the periodic superposition of the conjugated aromatic system. Two characteristic peaks of 3DA-CN are still detected in the SALa/CN photocatalyst, indicating that the introduction of SALa can not

introduce other La species. Significantly, the diffraction peak at the (002) plane of SALa/CN is obviously moved to a higher angle (from 27.67° to 27.82°) compared with 3DA-CN in the illustration of Fig. 3h. According to Bragg's law, the introduction of SALa decreases the layer spacing of 3DA-CN triggering the strong interaction between SALa and N (C) atoms [41,47]. Based on the decreased interlayer stacking distance together with La 3d XPS argon ion etching results, the introduced SALa locate the interlayer of 3DA-CN [48–50]. The changes in the functional groups of the photocatalysts were confirmed by Fourier transform infrared (FT-IR) spectra, and the corresponding results are presented in Fig. 3i. The signals at 810 cm^{-1} and 885 cm^{-1} are ascribed to the vibration mode of tri-s-triazine units in 3DA-CN [51,52]. To further clearly study the interaction between photocatalysts, the FT-IR spectra of as-prepared samples at 750–950 cm^{-1} are magnified in Fig. S5. The results show that the tri-s-triazine units in SALa/CN is migrated to a
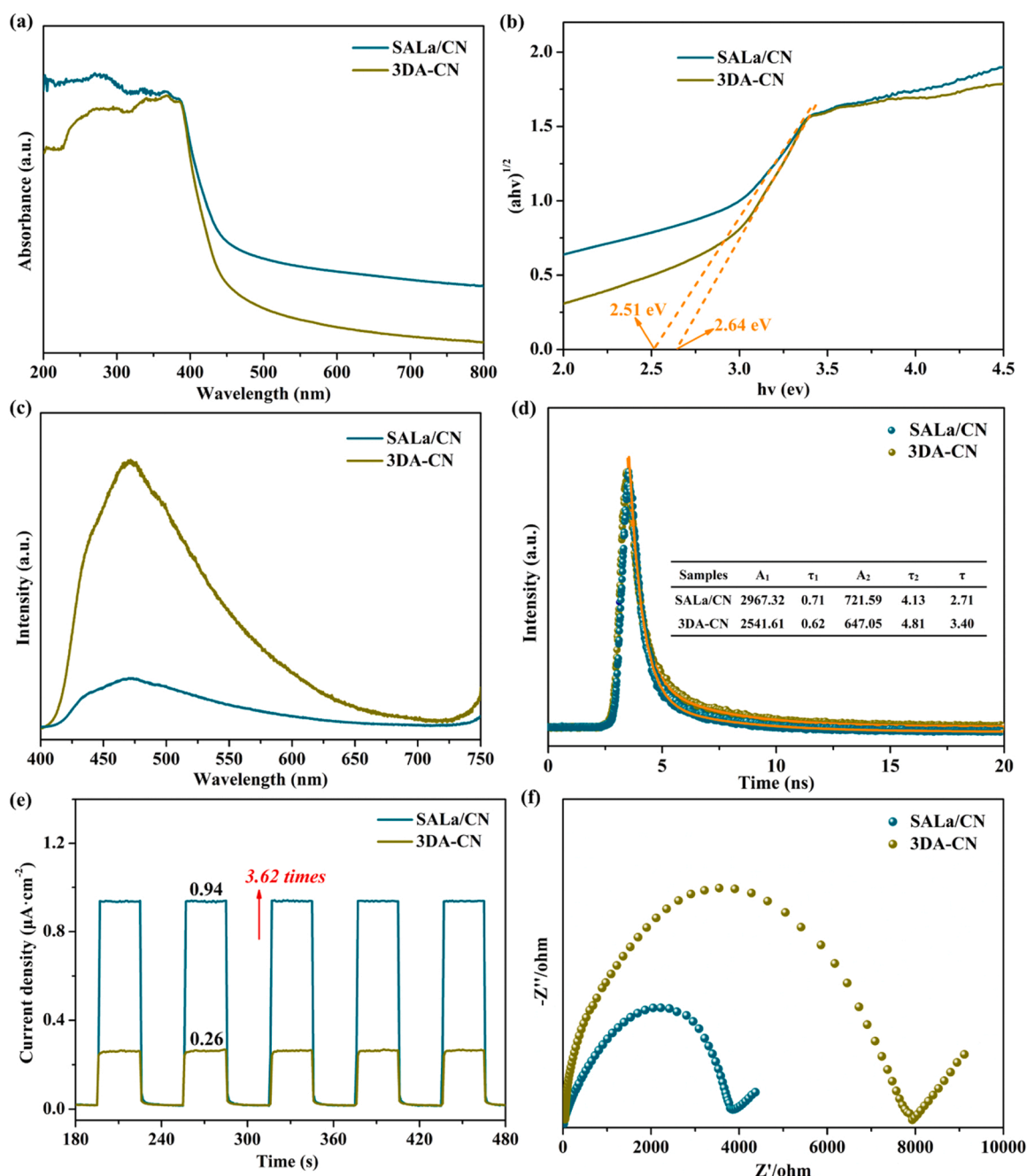

Fig. 4. (a) UV–vis DRS, (b) Tauc plots, (c) PL spectra, (d) TR-PL decay curves, (e) TPR and (f) Nyquist plots of 3DA-CN and SALa/CN.

higher wavenumber, indicating that SALa has been successfully introduced into the structure of 3DA-CN. The several vibration peaks at 980–1730 cm^{-1} are assigned to the C-N heterocycle, indicating the existence of a polymeric melon network for the as-prepared materials [53,54]. The region for 3040–3370 cm^{-1} has obvious characteristic peaks, which are mainly caused by the stretching vibration of the N-H functional groups of 3DA-CN.

3.3. Optical and photoelectrochemical properties

The light absorption properties of 3DA-CN and SALa/CN were characterized by UV–vis diffuse reflectance spectrometry (UV–vis DRS). As shown in Fig. 4a, 3DA-CN exhibits an inherent absorption peak at approximately 460 nm. An obvious red-shift is found in the absorption edge of SALa/CN compared with 3DA-CN. It indicates that the incorporation of SALa into the 3DA-CN lattice broadens the optical absorption ability. More importantly, the absorption peak of SALa/CN in the visible region is significantly enhanced. Therefore, the introduction of SALa improves the light utilization efficiency and provides the possibility for excellent properties of materials. The bandgaps of 3DA-CN and SALa/CN are plotted by the Kubelka–Munk theory in Fig. 4b. The bandgap (E_g) of SALa/CN (2.51 eV) is narrower than that of 3DA-CN (2.64 eV), meaning that SALa/CN needs lower energy to be excited in the process of the photocatalytic reaction [55].

Moreover, the optical parameters of the as-prepared photocatalysts in aqueous suspension were analyzed. The absorbances of 3DA-CN and SALa/CN are shown in Fig. S6. According to the Beer—Lambert law (Eq. (1)), the absorption coefficient (ε) is obtained.

$$A = -\lg\left(\frac{I}{I_0}\right) = \lg T = \varepsilon b c \tag{1}$$

where, A, I, I_0, T, b and c represent absorbance, transmitted light intensity, incident light intensity, transmittance, absorption layer thickness and concentration of light absorbing substance, respectively. The specific absorption coefficients ($\varepsilon *$) of 3DA-CN and SALa/CN are 875 and 2125 cm^2/g, respectively. The extinction coefficient (β) of the catalysts is calculated from the transmittance value using Eq. (2) and L_{cell} is the cell path length (m). The average extinction coefficients ($\beta *$) of 3DA-CN and SALa/CN obtained by performing linear regression over β are calculated to be 7250 and 14,500 cm^2/g, respectively. The relationship among the scattering coefficient ($\alpha *$), $\varepsilon *$ and $\beta *$ are presented in Eq. (3). The values of optical parameters are shown in Table S5.

$$\beta = 2.303 \left(-\frac{\lg T}{L_{cell}} \right) \tag{2}$$

$$\alpha^* = \beta^* - \varepsilon^* \tag{3}$$

$$\delta = h \times C \times \varepsilon^* \tag{4}$$

The optical thickness (δ) of 3DA-CN and SALa/CN is obtained in Eq. (4) (h: the height of liquid in the photocatalytic reaction system; C: the concentration of the photocatalyst). Therefore, the δ results for 3DA-CN and SALa/CN are 2.12 and 3.97, respectively. The δ values of 3DA-CN and SALa/CN conform to the optimum range of δ (1.8–4.4) in the photocatalytic system [56,57]. Moreover, the $\varepsilon *$ of SALa/CN is larger than that of 3DA-CN, which means that the introduction of SALa enhances the photocatalytic activity of the catalyst.

The effective separation of electrons and holes generated after semiconductor excitation is the key factor in improving material properties. Thus, the photoluminescence (PL) spectra of 3DA-CN and SALa/CN are analyzed in Fig. 4c. Compared with 3DA-CN, the addition of SALa significantly reduces the PL peak intensity of SALa/CN. It demonstrates that SALa/CN has excellent carriers separation efficiency. The position of the strongest emission wavelength (470 nm) of SALa/CN is slightly offset, which is caused by mutual electrons transfer to SALa and

3DA-CN [58,59]. Moreover, the lifetimes of photogenerated carriers are obtained by time-resolved photoluminescence (TR-PL) spectra in Fig. 4d. The spectra are analyzed by the double-exponential method using Eq. (5).

$$R(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \tag{5}$$

where, A_1, A_2, τ_1 and τ_2 are separately defined as the amplitude of the normalized decay ingredient and lifetime values. The average lifetime (τ_{ave}) values are calculated by Eq. (6).

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \tag{6}$$

As shown in the inlaid table of Fig. 4d, the carriers lifetime of SALa/CN is lower than that of 3DA-CN, indicating that the carriers can be effectively separated after the introduction of SALa [60,61]. The decrease in lifetime indicates that the main form of electrons transition is nonradiative transition and that electrons mainly participate in the photocatalytic reaction. Instead, electrons are returned to the ground state in the form of emitted photons and used to emit light in the excited state as radiation [62].

Transient photocurrent response (TPR) and electrochemical impedance spectroscopy (EIS) are significant characterization methods for the photoelectrochemical properties of materials. As depicted in Fig. 4e, the photocurrent intensity of SALa/CN (0.94 μA·cm^{-2}) is significantly increased about 3.62 times that of 3DA-CN (0.26 μA·cm^{-2}), indicating that the introduction of SALa obviously promotes the separation of electrons and holes [63,64]. Moreover, the Nyquist curves of 3DA-CN and SALa/CN are exhibited in Fig. 4f. It is well known that the smaller radius of EIS means the higher separation efficiency of carriers; consequently, SALa/CN has better charge separation efficiency than 3DA-CN [65,66]. Namely, SALa/CN has an excellent light utilization rate, high visible light absorption capacity and efficient carriers separation efficiency. Moreover, the specific surface area is an important factor affecting the photocatalytic activity of catalysts. Thus, N_2 adsorption/-desorption isotherm experiments were applied to measure the specific surface of 3DA-CN and SALa/CN. As shown in Fig. S7, the curves of the as-prepared samples clarify the typical IV isotherm with H_3 hysteresis loops, indicating that the pore structure of the materials is conducive to increasing the contact time with pollutants. SALa/CN (97.059 m^2/g) has larger specific surface area than 3DA-CN (92.478 m^2/g), indicating that the introduction of SALa provides more active sites for the reaction leading to higher degradation rates [67,68]. The specific surface area details of 3DA-CN and SALa/CN are summarized in Table S6.

3.4. Density functional theory (DFT) calculations

To investigate the advantages of SALa/CN catalyst with DLaN$_4$C$_2$ configuration, we studied the influence of SALa/CN and 3DA-CN on O_2 selectivity by DFT calculations and the optimized configurations of O_2 adsorption are presented in Fig. 5a-b. The computational details are presented in the SI (Section 4). The corresponding O_2 adsorption energy (E_{ads}) data are presented next to the corresponding configurations. The E_{ads} for 3DA-CN and DLaN$_4$C$_2$, models are −0.102 eV and − 0.504 eV, respectively. Moreover, superoxide free radical ($\bullet O_2^-$) plays major active specie in the photocatalytic reaction of this experimental system, and the corresponding investigations are presented in later capture experiments and ESR tests. Therefore, the feasibility of generating $\bullet O_2^-$ by O_2 adsorption on the as-prepared catalysts is discussed in Fig. 5c. Gibbs free energy (G) is a function of chemical thermodynamics used to determine the direction of process. The G could be calculated according to the same method as in the literature [69], in which G is calculated by Eqs. (7–8).

$$G_{gas} = H - TS = E_{ele} + ZPE + RT - TS \tag{7}$$

$$G_{solid} = H - TS = E_{ele} + ZPE - TS \tag{8}$$

L. Sun et al.

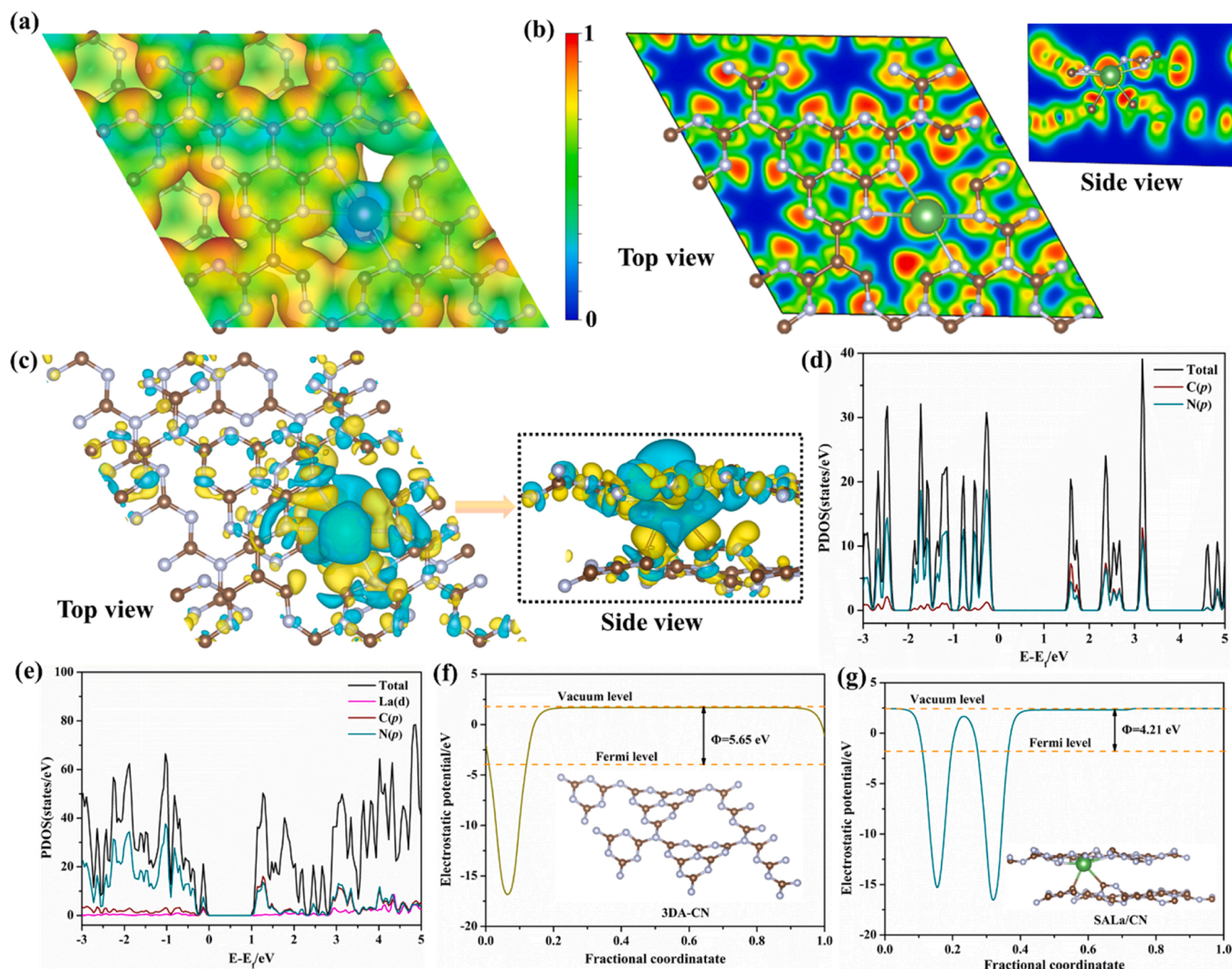*Applied Catalysis B: Environmental 338 (2023) 122979*

Fig. 6. (a) ESP of SALa/CN with an isosurface of 0.02 e/Bohr^3; (b) ELF of SALa/CN and (c) EDD of SALa/CN with an isosurface of 0.002 e/Å^3; (d, e) The DOS of 3DA-CN and SALa/CN; (f, g) work function of 3DA-CN and SALa/CN by DFT calculations.

3.5. Photocatalytic activity tests

3.5.1. Photocatalytic degradation of antibiotic experiments

To detect the synergistic effect of the improved strategy, the photocatalytic degradation of TC (20 mg/L, 100 mL) was carried out under simulated sunlight ($\lambda > 420$ nm). The specific experimental implementation process has been mentioned in Section 2.4. The degradation efficiency (DE) can be calculated by Eq. (9) for the concentration of TC in the solution for t minutes (C_t) and the initial concentration of TC (C_0).

$$DE\left(\%\right) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{9}$$

As shown in Fig. 7a, the photocatalytic activity of SALa/CN (98.38%) is significantly increased compared with that of 3DA-CN (31.90%). Meanwhile, the TC removal activity of SALa/CN is better than that of most g-C$_3$N$_4$-based photocatalysts compared with previous reported studies (Table S7). The introduction of SALa realizes the effective separation of electrons and holes in space and enhances the utilization rate of visible light. Moreover, SALa provides a new site for O$_2$ activation and special coordination structure, which makes the as-prepared material highly selective to O$_2$, so that more active species (•O$_2^-$) can act on pollutant molecules and thus efficiently remove pollutants. The corresponding kinetic constants (k), fitted by a first-order kinetic model, for quantitative comparison are depicted in Fig. 7b. SALa/CN exhibits the

larger slope than 3DA-CN, meaning that it has excellent photocatalytic activity relative to 3DA-CN. The k values of 3DA-CN and SALa/CN are presented in the illustration of Fig. 7b. The k value of SALa/CN (0.10661 min^{-1}) achieves 9.81 times than that of 3DA-CN (0.01087 min^{-1}). Therefore, the introduction of SALa is an effective strategy to improve photocatalyst activity. Total organic carbon (TOC) characterization was applied to evaluate the mineralization performance of the SALa/CN photocatalytic system for TC. As shown in Fig. S9, the SALa/CN displays the excellent removal rate (73.27%) in 30 min implying that SALa/CN has fantabulous mineralization activity for TC. The high rate of mineralization means that SALa/CN has the ability to convert TC into small pollutant-free molecules (CO$_2$, H$_2$O, etc.) [79,80]. To study the applicability of SALa/CN for the removal of other antibiotics, photocatalytic degradation experiments of oxytetracycline hydrochloride (OTC) and doxycycline hydrochloride (DOX) were performed. As shown in Fig. 7c, the degradation efficiency of OTC and DOX by the SALa/CN photocatalyst reached 84.49% and 91.71% within 30 min, respectively. It indicates that SALa/CN has generally excellent photocatalytic activity for the removal of antibiotics. Moreover, we simulated the degradation of TC by SALa/CN in the real environment with water from Xuanwu Lake in Nanjing and tap water from the laboratory. In real water environment, SALa/CN material still shows fantabulous photocatalytic performance in Fig. 7d, with degradation rates of 92.51% and 94.66% in lake water and tap water, respectively.
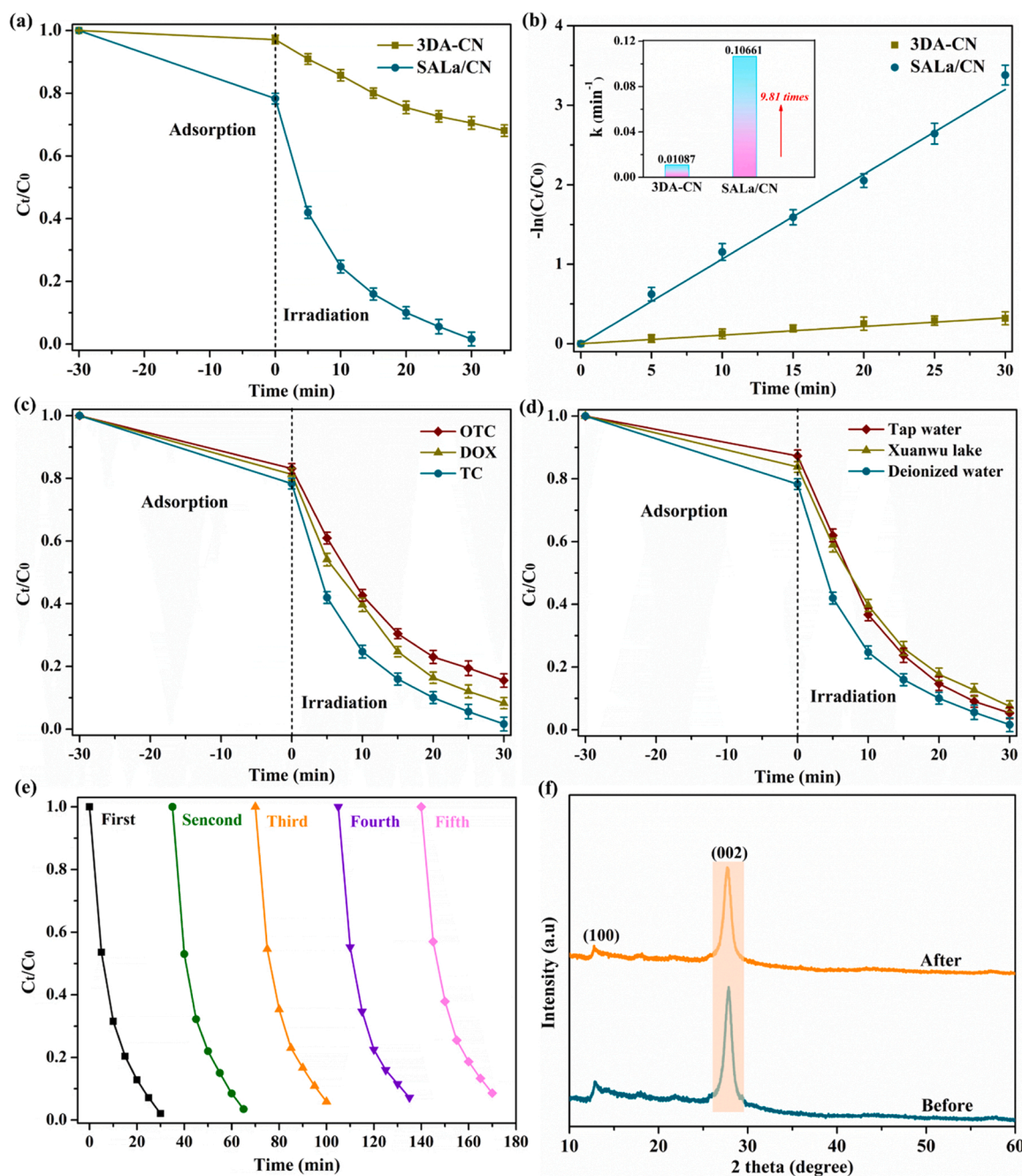
Fig. 7. (a) Time-concentration plots; (b) pseudo-first-order kinetic curves (inset apparent reaction rate constant k) for photocatalytic degradation of TC; (c) photocatalytic degradation of different organic pollutants, (d) real water environment degradation and (e) cycle degradation experiments of SALa/CN; (f) XRD patterns of SALa/CN before and after cycle experiments.

From what has been discussed above, SALa/CN has high efficiency and practical application value in treating sewage antibiotics.

The reusability and durability of photocatalysts is an important factor in evaluating the practical application of photocatalysts. Five cycles were used to evaluate the indicator and the results are shown in Fig. 7e. The SALa/CN photocatalyst still has good photocatalytic activity after five cycles and the degradation efficiency is decreased slightly, which might be due to a certain amount lost in the process of collecting the catalyst after the cycle experiments. To study whether the morphology and crystal structure of SALa/CN changed after the cyclic experiment, AC-HAADF-STEM and XRD were performed. As depicted in Fig. S10, the AC-HAADF-STEM result of SALa/CN after the cycling experiment still presents scattered single atoms, and no agglomeration

clusters or particles are found, which reveals that SALa embedded in 3DA-CN is stable in the photocatalytic process. Moreover, SALa/CN was detected with the same crystal structure as before the reaction in Fig. 7f. The above experiments and characterizations prove that SALa/CN has excellent reusability and durability and possesses certain potential in practical applications.

3.6. Mechanism investigations

It is essential to explore the active species in which photocatalytic systems operate. Therefore, active species trapping experiments were applied to study the mechanism for the degradation of TC by SALa/CN. Specifically, ascorbic acid (AA), ethylenediaminetetraacetic acid

disodium (EDTA-2Na), L-tryptophan, catalase (CAT) and isopropanol (IPA) are used as trapping agents to capture superoxide radical ($\bullet O_2^-$), holes (h^+) single oxygen ($^1O_2$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($\bullet OH$), respectively [21,81,82]. As clarified in Fig. 8a, the degradation activity of SALa/CN (22.67%) is substantially suppressed after the addition of AA, which indicates that $\bullet O_2^-$ is the dominant active species in the photocatalytic reaction process. The addition of L-tryptophan makes the degradation efficiency of TC by SALa/CN only 31.02%, indicating that $^1O_2$ is also one of the decisive active species involved in the photocatalytic degradation reaction. In contrast, the photocatalytic degradation efficiency of TC (89.04%) is hardly decreased by combining with IPA, illustrating that $\bullet OH$ plays a minor role in the degradation process. Moreover, the TC degradation efficiency decreased to 40.74% when the h^+ was captured by EDTA-2Na. The

degradation efficiency of SALa/CN shows a downward trend (70.91%) after capturing H_2O_2 by CAT. Hence, it is obvious that the contribution degree of active species is in the order of $\bullet O_2^- > {}^1O_2 > h^+ > H_2O_2 > \bullet OH$.

To further declare the presence of free radicals in the degradation system of SALa/CN, the electron spin resonance (ESR) tests were performed and the corresponding results are shown in Fig. 8b-d. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperi-done (TEMP) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were used as capture agents to separately capture $\bullet O_2^-$, $^1O_2$ and h^+. As depicted in Fig. 8b, the characteristic peak of DMPO-$\bullet O_2^-$ is not detected signal under darkness, although significant signal peaks are detected under visible light. SALa/CN exhibits the higher signal peak than 3DA-CN. It indicates that SALa effectively activates more oxygen (O_2) to
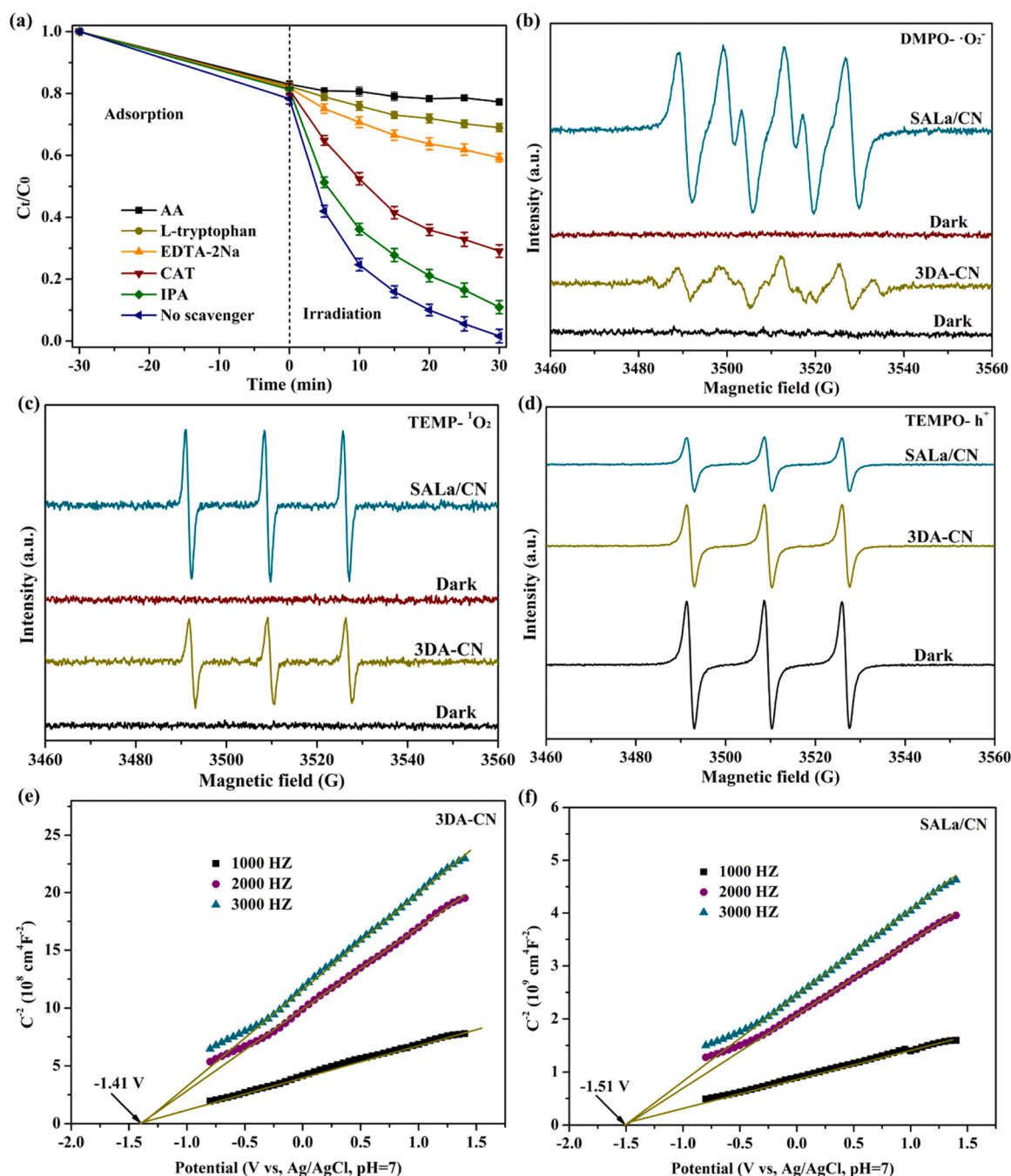

Fig. 8. (a) The trapping experiments of SALa/CN; (b-d) ESR spectra of the as-prepared photocatalysts; (e, f) Mott-Schottky plots of 3DA-CN and SALa/CN.

produce $\bullet O_2^-$ and thus SALa/CN has excellent photocatalytic performance [32,83]. In addition, the TEMP -$^1O_2$ peak intensity of SALa/CN is obviously stronger than that of 3DA-CN, indicating that SALa is beneficial to the production of more $^1O_2$ and thus $^1O_2$ is used to break down pollutant molecules [84]. The relative peak magnitude is 1:1:1 (Fig. 8d) corresponding to TEMPO ~ h^+. The signal peaks are detected in the dark, due to the presence of a single electron in the capture reagent (TEMPO). Noticeably, the signal peaks are decreased under visible light irradiation, signifying that the as-prepared materials can generate h^+ to neutralize the lone pair electrons of TEMPO [85]. Moreover, the introduction of SALa promotes the generation of h^+, which means that SALa/CN can produce more h^+ to act on pollutant molecules in the process of photocatalytic treatment for antibiotics. Therefore, $\bullet O_2^-$, $^1O_2$

and h^+ are the main active substances in this photocatalytic process, which is consistent with the results of the capture experiments.

To investigate the valence band (VB) and conduction band (CB) positions of the as-prepared samples, Mott-Schottky (M-S) tests were conducted in Fig. 8e. The CB positions of 3DA-CN and SALa/CN are − 1.21 V and − 1.31 V, respectively. The position of the CB is obviously moved up, which facilitates the production of $\bullet O_2^-$. The E_g values of 3DA-CN (2.64 eV) and SALa/CN (2.51 eV) were obtained by the Kubelka–Munk theory in Fig. 4b. The introduction of SALa decreases the E_g of 3DA-CN promoting the light absorption. Therefore, the VB positions of the 3DA-CN (1.43 V) and SALa/CN (1.20 V) were obtained according to the formula $E_{VB} = E_{CB} + E_g$ [86]. To further verify the correctness of the CB and VB positions, VB-XPS spectra are applied to
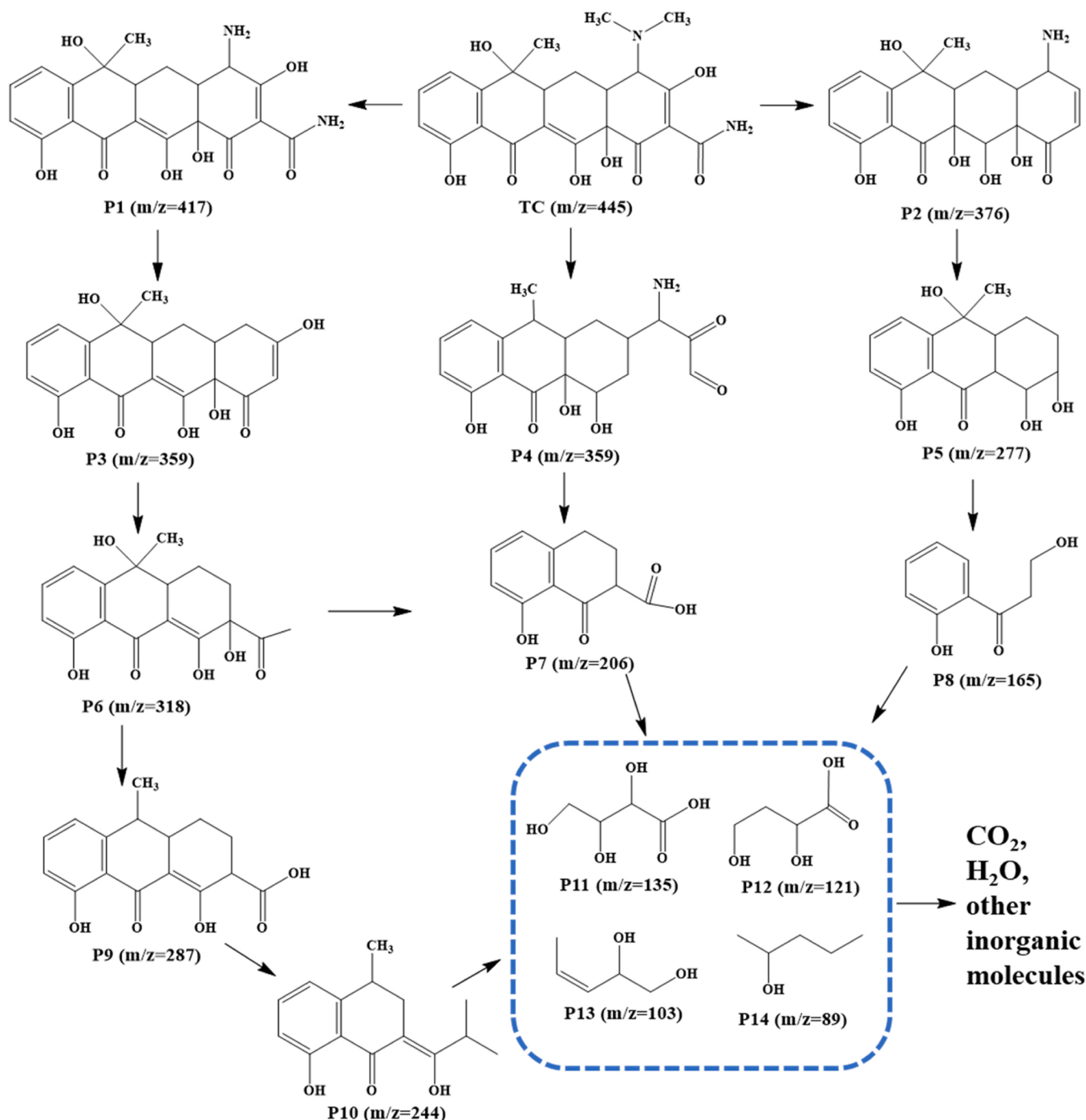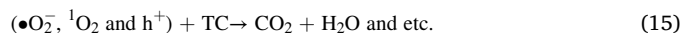

Fig. 9. The possible degradation pathway of TC molecule during the removal process.

deduce the VB positions. As illustrated in Fig. S11, the VB-XPS spectra detection positions of 3DA-CN and SALa/CN are 1.26 eV and 1.03 eV, respectively. The test data need to be converted according to the formula $E_{NHE}/V = 4.63 + f - 4.44$ (E_{NHE}: standard hydrogen electrode potential; f: sample VB test location) [46]. Therefore, the real E_{VB} of 3DA-CN and SALa/CN are 1.45 V and 1.22 V, respectively, which are consistent with those described above. The detailed band structure diagrams of 3DA-CN and SALa/CN are described in Fig. S12.

The possible degradation pathways and intermediates of TC were proposed by liquid chromatography—mass spectrometry (LC—MS). The LC—MS results of photocatalytic reaction for 0, 10, 20 and 30 min are shown in Fig. S13. It is evident that the photocatalytic reaction begins with a strong peak at $m/z = 445$, corresponding to the protonated TC molecule. New peaks are detected with the increasing reaction time, meaning that TC was broken down into other intermediates. Moreover, the peak of TC is decreased and almost disappeared at 30 min. The new signal peaks were found at 10 min, but disappeared or decreased at 20 min and 30 min. Moreover, some lower m/z signals were produced or significantly increased. It suggests that intermediates can be further destroyed and eventually broken down into CO_2, H_2O and other small molecules. In combination with the LC—MS diagram results and relevant literatures, the possible TC degradation paths of SALa are presented in Fig. 9. Firstly, The TC was decomposed into P1 ($m/z = 417$) after demethylation via $\bullet O_2^-$ and $^1O_2$ oxidation processes [87]. P1 molecules undergo the elimination and deamidation reactions under the action of $\bullet O_2^-$ and h^+ to produce P3 ($m/z = 359$) [79]. P3 is fragmented to P6 ($m/z = 318$) by demethylation and ring-opening. Intermediate product P6 can be attacked by h^+ leading to the formation of product P9 ($m/z = 287$) by dehydration reaction. And P9 is further decomposed to P10 ($m/z = 244$) with the loss of carbonyl groups. Meanwhile, TC can be amidated to form P2 ($m/z = 376$) and is also demethylated and ring-opened to produce P4 ($m/z = 359$). Intermediate P7 ($m/z = 206$) can be generated by breaking the cyclic hydrocarbon structure of P4. P5 ($m/z = 277$) and P8 ($m/z = 165$) can be obtained from cyclic hydrocarbon structure fractures. The above intermediate products are further decomposed into ring-opening products (P11 ($m/z = 135$), P12 ($m/z = 121$), P13 ($m/z = 103$) and P14 ($m/z = 89$)) with the oxidation of the benzene ring structure. Eventually, these products are further mineralized into CO_2, H_2O and other small molecules [88].

Through the above investigations, a possible mechanism of TC degradation is proposed (Fig. 10). The introduction of SALa improves the absorption capacity of the photocatalyst for visible light, and SALa/

CN requires lower energy to excite producing electrons and holes (Eq. (10)). The CB position of SALa/CN is located at −1.31 V vs normal hydrogen electrode (NHE), which is more negative than the redox potential of $O_2/\bullet O_2^-$ (−0.33 V vs NHE). The electrons are migrated from the VB of SALa/CN to the CB, where electrons combine with O_2 to form $\bullet O_2^-$ (Eq. (11)). Moreover, SALa acts as an active site enhancing the ability to activate O_2 and can be used as a bridge to transfer electrons from the catalyst support to the O_2 promoting charge transfer and separation. $DLaN_4C_2$ has a more negative G value resulting in the easier formation of $\bullet O_2^-$. The special bilayer coordination structure promotes the effective separation of charge in space, thus achieving efficient photocatalytic activity. Furthermore, $\bullet O_2^-$ can react with h^+ to generate $^1O_2$ (Eq. (12)) and react with H^+ to form H_2O_2 (Eq. (13)). The h^+ can directly react with H_2O in solution to form O_2 providing the raw material for the main reactive species (Eq. (14)) and can also act directly on pollutant molecules (Eq. (15)). The capture experiments and ESR tests clarified that $\bullet O_2^-$, $^1O_2$ and h^+ are the main active species to remove TC and convert TC into some pollution-free small molecules (Eq. (15)).

$$SALa/CN + hv \rightarrow h^+ + e^- \tag{10}$$

$$O_2 + e^- \rightarrow \bullet O_2^- \tag{11}$$

$$\bullet O_2^- + h^+ \rightarrow {}^1O_2 \tag{12}$$

$$\bullet O_2^- + e^- + 2\,H^+ \rightarrow H_2O_2 \tag{13}$$

$$2\,H_2O + 4\,h^+ \rightarrow O_2 + 4\,H^+ \tag{14}$$

$$(\bullet O_2^-, {}^1O_2 \text{ and } h^+) + TC \rightarrow CO_2 + H_2O \text{ and etc.} \tag{15}$$

4. Conclusions

In summary, a high loading rare earth SALa bridge on 3DA-CN achieving the effective separation of charge in space has been designed for efficient photocatalytic activity. AC-HAADF-STEM, XANES and EXAFS elucidate that SALa has been successfully introduced into 3DA-CN, and that the coordination configuration with 3DA-CN is the $DLaN_4C_2$ configuration. DFT calculations suggest that the $DLaN_4C_2$ (−0.042 eV) configuration is more likely to generate $\bullet O_2^-$ than the 3DA-CN (0.281 eV) from a thermodynamic perspective. It means that the as-prepared single-atom catalyst has excellent ability to activate O_2 and more efficient selectivity for the generation of $\bullet O_2^-$. UV–vis DRS, PL, TR-
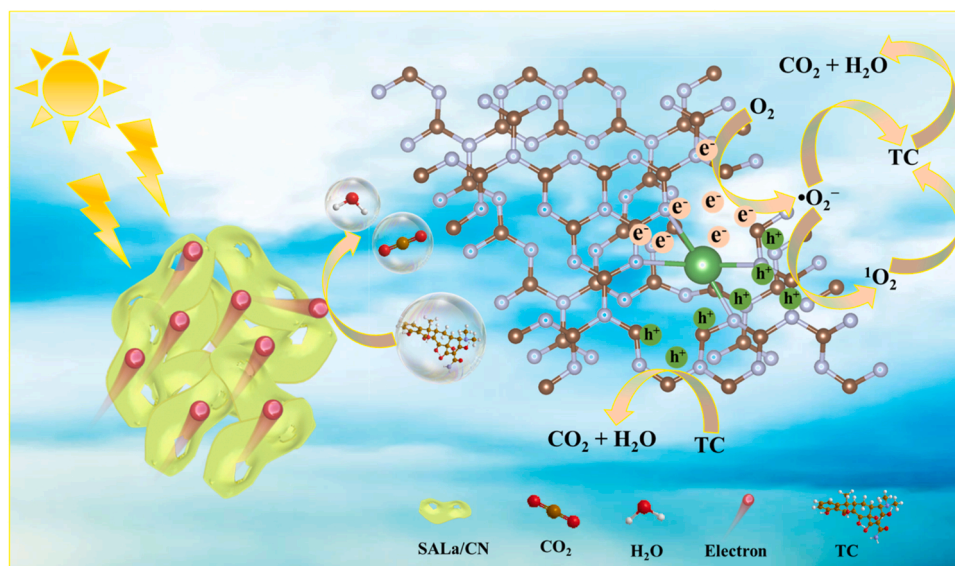

Fig. 10. The proposed photocatalytic degradation mechanism of SALa/CN for TC.

PL and electrochemical experiments have clarified that SALa/CN exhibits excellent visible light utilization and efficient carriers separation efficiency. SALa/CN shows excellent antibiotic degradation activity, and the degradation rates of TC, OTC and DOX are 98.38%, 84.49% and 91.71% within 30 min, respectively. The k value of SALa/CN (0.10661 min^{-1}) for TC achieves 9.81 times than that of 3DA-CN (0.01087 min^{-1}). Trapping experiments and ESR devices prove that the contribution of active species in the photocatalytic TC removal process is $\bullet O_2^- > {}^1O_2 > h^+ > H_2O_2 > \bullet OH$. This study provides a method for the preparation of rare earth single atom photocatalysts with high loads, and provides a deeper understanding about the mechanism of electron separation for rare earth SALa in space.

CRediT authorship contribution statement

Linlin Sun: Investigation, Methodology, Formal analysis, Data curation, Validation, Conceptualization, Writing – review & editing. **Xiaoshuo Liu:** Methodology, Conceptualization, Data curation, Writing–review & editing. **Yibing Feng:** Investigation, Visualization. **Xunlei Ding:** Validation, Software, Methodology. **Jigang Wang:** Writing – review & editing, Project administration, Funding acquisition. **Nan Jiang:** Methodology, Conceptualization, Visualization. **Shanjiang Wang:** Writing – review & editing, Data curation, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgement

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.122979.

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